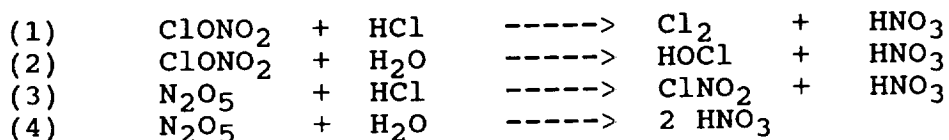


LABORATORY STUDIES OF STICKING COEFFICIENTS AND  
 HETEROGENEOUS REACTIONS IMPORTANT IN THE STRATOSPHERE

Ming-Tau Leu

Jet propulsion Laboratory, California Institute of Technology,  
 4800 Oak Grove Drive, Pasadena, California 91109.

The discovery of ozone depletion during springtime in the Antarctic stratosphere has received wide spread attention. Both meteorological and chemical mechanisms have been used in attempts to explain this observation. The chemical theory focused on the chlorofluoromethanes released into the atmosphere. However, gas-phase, homogeneous reactions alone in the model can not adequately explain such a depletion. Heterogeneous reactions, such as:



on ice surfaces could be important in the Antarctic stratosphere. Reactions (1)-(4) are thought to convert  $\text{ClONO}_2$  and  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$  in the solid phase while  $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{ClNO}_2$  are released into the stratosphere as gas-phase products. The photolysis of  $\text{Cl}_2$ ,  $\text{HOCl}$ , and  $\text{ClNO}_2$ , then produces active chlorine which subsequently removes ozone through several catalytic cycles, including the  $\text{Cl}_2\text{O}_2$  mechanism. The polar stratospheric clouds are thought to consist of mixtures of water ice, nitric acid, and sulfuric acid. Condensation of  $\text{HCl}$  onto the PSC's could provide active surfaces for heterogeneous reactions, such as (1) and (3).

A fast flow reactor was used for investigating the sticking coefficients of the trace gases on ice. The diameter of the flow tube was 1.89 cm, and the length was 50 cm. The temperature of the flow tube was measured by a pair of thermocouples and its temperature was maintained at about 190-200 K by circulating cooled dry nitrogen through its outside jacket. The cooling jacket was further insulated by another exterior jacket which was evacuated by a mechanical pump. The pressure was monitored at the downstream end of the flow tube by means of a Baratron pressure meter. The ice surface was prepared by passing water vapor in helium carrier through an injector tube which was slowly moved along the length of the flow tube until a thin uniform ring was formed. Ice was prevented from forming in the injector tube by flowing dry nitrogen through a jacket which extended beyond its downstream end. The flow rate of water vapor was measured by monitoring the pressure and the temperature at the water reservoir and also monitoring the helium flow rate. The detection of the trace gases was performed by using an EMBA II

quadrupole mass spectrometer. We utilized the electron impact ionization method to monitor the parent peak or the fragmentation peaks of the gas molecules. For example, H<sub>2</sub>O or HCl were detected by their parent peaks while ClONO<sub>2</sub> or N<sub>2</sub>O<sub>5</sub> were measured by NO<sub>2</sub> ions.

Measurements of sticking coefficients for H<sub>2</sub>O, HCl, Cl<sub>2</sub> and HNO<sub>3</sub> on ice and of reaction probabilities for reactions (1) and (2) have been summarized in a recent publication. Measured sticking coefficients are: 0.3 (+0.7, -0.1) for H<sub>2</sub>O, 0.4 (+0.6, -0.4) for HCl,  $< 1.0 \times 10^{-4}$  for Cl<sub>2</sub>, and 0.3 (+0.7, -0.3) for HNO<sub>3</sub> at 200 K. The reaction probability of ClONO<sub>2</sub> on ice was found to be 0.06 ( $\pm 0.03$ ) while HOCl was observed as the sole product in the gas phase. In the presence of 0.015-0.071 mole fractions of HCl in ice, the reaction probability of ClONO<sub>2</sub> is greatly enhanced, approaching 0.27 (+0.73, -0.13) while molecular chlorine was found to be the major product in the gas phase. Another reaction product was nitric acid which remained in the solid phase.

In a preliminary investigation the reaction probability of N<sub>2</sub>O<sub>5</sub> was found to be  $2.8 (\pm 1.1) \times 10^{-2}$  on ice at 195 K and  $3.4 (\pm 1.4) \times 10^{-2}$  with 0.015-0.040 mole fractions of HCl at 195 K. One of the reaction products, HNO<sub>3</sub>, remained in the condensed phase. It should be noted that the yield of NO<sub>2</sub>, a probable reaction product, was negligible in these N<sub>2</sub>O<sub>5</sub> reactions. This work will be continued in the laboratory and the results will be presented at the Workshop.

In addition, similar reactions on sulfuric acid/water ice surfaces will be investigated because of their potential importance for the global stratosphere.

Acknowledgments. The research described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

#### References:

1. J. C. Farman, B. G. Gardiner, and J. D. Shanklin, *Nature*, **315**, 207 (1985).
2. M-T. Leu, *Geophys. Res. Lett.*, **15**, 17 (1988).
3. *Geophysical Research letters*, November Supplement (1986).
4. M. B. McElroy, R. J. Salawitch, S.C. Wofsy, and J. A. Logan, *Nature*, **321**, 759 (1986).
5. L. T. Molina and M. J. Molina, *J. Phys. Chem.*, **91**, 433 (1987).
6. S. Solomon, R. R. Garcia, F. S. Rowland, and D. J. Wuebbles, *Nature*, **324**, 755 (1986).
7. M. A. Tolbert, M. J. Rossi, R. Malhotra, and D. M. Golden, *Science*, **238**, 1258 (1987).
8. M. J. Molina, T-L Tso, L. T. Molina, and F. C. Wang, *Science*, **238**, 1253 (1987).